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Research Articles

Prebiotic Chemistry of Pluto

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Abstract

We present the case for the presence of complex organic molecules, such as amino acids and nucleobases, formed by abiotic processes on the surface and in near-subsurface regions of Pluto. Pluto's surface is tinted with a range of non-ice substances with colors ranging from light yellow to red to dark brown; the colors match those of laboratory organic residues called tholins. Tholins are broadly characterized as complex, macromolecular organic solids consisting of a network of aromatic structures connected by aliphatic bridging units (*e.g.,* Imanaka *et al.,* 2004; Materese *et al.,* 2014, 2015). The synthesis of tholins in planetary atmospheres and in surface ices has been explored in numerous laboratory experiments, and both gas- and solid-phase varieties are found on Pluto. A third variety of tholins, exposed at a site of tectonic surface fracturing called Virgil Fossae, appears to have come from a reservoir in the subsurface. Eruptions of tholin-laden liquid H_2O from a subsurface aqueous repository appear to have covered portions of Virgil Fossae and its surroundings with a uniquely colored deposit (D.P. Cruikshank, personal communication) that is geographically correlated with an exposure of H_2O ice that includes spectroscopically detected NH_3 (C.M. Dalle Ore, personal communication). The subsurface organic material could have been derived from presolar or solar nebula processes, or might have formed *in situ*. Photolysis and radiolysis of a mixture of ices relevant to Pluto's surface composition (N_2, CH_4, CO) have produced strongly colored, complex organics with a significant aromatic content having a high degree of nitrogen substitution similar to the aromatic heterocycles pyrimidine and purine (Materese *et al.,* 2014, 2015; Cruikshank *et al.,* 2016). Experiments with pyrimidines and purines frozen in H_2O-NH_3 ice resulted in the formation of numerous nucleobases, including the biologically relevant guanine, cytosine, adenine, uracil, and thymine (Materese *et al.,* 2017). The red material associated with the H_2O ice may contain nucleobases resulting from energetic processing on Pluto's surface or in the interior. Some other Kuiper Belt objects also exhibit red colors similar to those found on Pluto and may therefore carry similar inventories of complex organic materials. The widespread and ubiquitous nature of similarly complex organic materials observed in a variety of astronomical settings drives the need for additional laboratory and modeling efforts to explain the origin and evolution of organic molecules. Pluto observations reveal complex organics on a small body that remains close to its place of origin in the outermost regions of the Solar System. Key Words: Pluto—Tholin—Ice—Nucleobase. Astrobiology 19, 831–848.

1. Introduction

The investigation of the composition and physical properties of Pluto began with the first detection of frozen methane in 1976 (see review by Cruikshank *et al.,* 2015) and continues with the study of data obtained by the New Horizons spacecraft during a close flyby of the planet in 2015 (Stern *et al.,* 2015). Discoveries of the molecular composition of the surface and the atmosphere establish the basis for a discussion of the origin and evolution of the planet, including possible prebiotic chemistry, defined as the synthesis of significant amounts of biologically important molecules, such as

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sugars, lipids, amino acids, or nucleobases, via abiotic processes. A number of observational and theoretical results bear on this issue, as we describe here.

In outline, we first present an overview of the characteristics of Pluto's atmosphere and surface derived from nearly four decades of astronomical studies from Earth and from the close-up investigation of Pluto, its satellites, and the space environment with the New Horizons spacecraft. Second, we consider Pluto's atmospheric and surface chemistry as it relates to the origin and composition of the colored component of the surface, and the distribution of the main volatile components (N_2, CO, and CH_4) present as ices. The distribution of these materials is closely related to the geological structures revealed on Pluto by the New Horizons spacecraft. In addition, we discuss the discovery and significance of H_2O ice containing NH_3 in limited regions on Pluto's surface, including the age, relationship to the red coloring agent, and possible means of emplacement. In terms of chemical composition broadly defined, there appears to be a connection of the colored components of Pluto's surface, presumed to be refractory organic complexes (tholins), to the organic components in the interstellar medium and the solar nebula. We also describe the results of the synthesis of tholins in the laboratory from the energetic processing of a mixture of molecular ices known to occur on the planet. Finally, we speculate on the occurrence of nucleobases of prebiotic interest in the organic and volatile constituents of Pluto's surface and the implications for other small bodies in the outer Solar System.

In this paper we frame a scenario in a geological context in which complex organic material is formed in the surface ices and potentially in fluid reservoirs in the near subsurface. The latter scenario is motivated by the New Horizons finding that in some regions of the surface specific geological structures are sites of both complex organics and H_2O ice. The presence of complex organics embedded in H_2O ice is especially interesting to astrobiology if their components include compounds with molecular structures characteristic of purines ($C_5H_4N_4$) and pyrimidines ($C_4H_4N_2$). Radiation processing of purines and pyrimidines embedded in H_2O-NH_3 ice can lead to the formation of a number of biological and nonbiological nucleobases, as shown in recent laboratory experiments (Nuevo *et al.,* 2009, 2012, 2014; Materese *et al.,* 2013, 2017) and theoretical studies (Bera *et al.,* 2010, 2016) described below.

2. Atmospheric Chemistry—Volatiles and Tholins

Pluto has a tenuous atmosphere with a surface pressure of $\sim 11\,\mu$bar (1.1 Pa) and is primarily composed of N_2, CH_4, and CO. Additional molecules are formed in the atmosphere by UV photolysis, including C_2H_2, C_2H_4, C_2H_6, HCN, C_4H_2, and HC_3N, which precipitate in molecular form onto the surface. The three C_2 hydrocarbons are the most abundant (*e.g.,* Krasnopolsky and Cruikshank, 1999; Zhu *et al.,* 2014; Gladstone *et al.,* 2016; Gao *et al.,* 2017; Wong *et al.,* 2017; Young *et al.,* 2018) and play an important role in the hydrocarbon chemistry and aerosol formation in Pluto's atmosphere (Luspay-Kuti *et al.,* 2017). These materials, as well as larger organic molecules formed by photolysis induced by solar and interplanetary UV flux, aggregate into relatively refractory particles that form as many as 20 layers of haze in the atmosphere, eventually precipitating onto the surface (Wong *et al.,* 2017; Gao *et al.,* 2017), further enriching the chemical diversity of the surface (Cheng *et al.,* 2017). Estimates of the settling time of these particles and the rate of deposition on the surface suggest that if the present rates were typical of Pluto's atmospheric history, a layer ~ 3.5 m deep should be accumulated in 10^9 years (Grundy *et al.,* 2018). Grundy *et al.* (2018) considered the role that the accumulated layer might play in Pluto's geological history. A steady-state production and surface accumulation rate in the present epoch would render Pluto's surface uniform in color and albedo. The surface is clearly not uniform (Fig. 1), showing a range over a factor of ten in absolute reflectance and vivid colors ranging from white through pale yellow, to red, brown, and very dark brown. If precipitating haze particles interact with the existing surface materials either through chemical reactions, sintering in regions of higher temperature (a region called Cthulhu[1] may get as warm as $T = 72$ K in some seasons when Pluto is at perihelion), or otherwise changing their basic optical characteristics, there may be a way to rationalize the planet's appearance with its atmospheric history. Another explanation may be found in the long-term temporal variability of the atmosphere and its level of haze production, a scenario in which UV radiation reaches the surface at times of atmospheric transparency when the mixing ratio of CH_4 relative to N_2, the principal atmospheric gas, is reduced.

Methane in Pluto's atmosphere effectively blocks Lyman-α (Ly-α) UV light from reaching the surface, but is transparent to longer wavelength UV. Because of Pluto's long-term seasonal cycles as well as secular changes, the Ly-α opacity of the atmosphere at the present time is unlikely to be the same as it has been in past epochs or as it may be in the future (Earle and Binzel, 2015; Stern *et al.,* 2017; Bertrand *et al.,* 2018). Bertrand *et al.* (2019) have shown that, during the cycles of Pluto's seasons and on 30-My timescales, through the exchange of CH_4 and N_2 between the atmosphere and the surface by condensation and evaporation, the mixing ratio of CH_4 in the atmosphere varies widely. Consequently, simulations show that for extended periods the atmosphere is partially transparent to UV radiation, varying from 10% to 0.01% transmission. In addition to the solar UV flux, there is a second source of resonant scattered Lyman-α radiation of comparable flux from the interplanetary medium (Gladstone *et al.,* 2018). Together, the solar and interplanetary Lyman-α flux is $\sim 3.4 \times 10^8$ photons/cm^2/s. Especially during times of maximum transparency ($\sim 10\%$) to UV light, photolysis of the surface ices may have significantly affected the chemical transformation of small molecules into larger molecular complexes, termed tholins, on short timescales of order 10^5 to 10^6 y (D.P. Cruikshank *et al.,* personal communication).

Tholins are presumed to be an important naturally occurring component of both the atmosphere and surface of Pluto. They are solid materials that can be created in the laboratory and are broadly characterized as relatively refractory (*i.e.,* stable at $T > 100$ K) organic complexes produced by energetic processing of simpler carbon-bearing and other molecules in the gas or solid phase. They are disordered polymer-like materials made of repeating chains of linked

[1]Some place names used here are informal.

FIG. 1. Pluto's surface imaged with New Horizons (enhanced color). This is the hemisphere viewed in greatest detail by the spacecraft cameras and spectrometers at the flyby of July 14, 2015. This full-disk image resolves surface features as small as ~1.3 km. The large, smooth plain just to the right of the center of the disk is Sputnik Planitia, a convecting layer of solid N_2 whose surface is covered with yellow tholin material currently precipitating from the atmosphere. NASA image PIA19952.

subunits and complex combinations of functional groups. Gas-phase tholins were initially studied in the context of organic solids in the interstellar medium, the clouds of Jupiter, and the atmosphere of early Earth (Sagan and Khare, 1971a, 1971b; Khare and Sagan, 1973). Subsequently, Khare *et al.* (1981, 1984a) showed that colored particles are made by UV photolysis of CH_4 and N_2 in simulated Titan atmosphere conditions. While the complex refractive indices of this ''Titan tholin'' published by Khare *et al.* (1984b) have been used in modeling the spectra of many planetary bodies, the analytical techniques available at the time were unable to reveal the full details of its complex structure (*e.g.,* Khare *et al.,* 1981).

Atmospheric tholins have long been considered a potentially interesting source of prebiotic chemistry (see the review by Cable *et al.,* 2012). Early analyses of Titan-like tholins (created from spark discharge experiments in a mixture of N_2:CH_4 (0.9:0.1) revealed the presence of pyridines, pyrimidines, and nitriles (Khare *et al.,* 1981). Amino acids were formed when Titan tholins were dissolved in acidic water (Khare *et al.,* 1986). These early experiments demonstrated the potential for the formation of a wide range of biological and nonbiological amino acids in planetary environments, and indeed, a wide variety of amino acids are found in primitive carbonaceous meteorites and interplanetary dust (Pizzarello *et al.,* 2006). Hydrolysis of Titan tholins made by spark discharge in a mixture of N_2:CH_4 (0.95:0.05) can occur rapidly, producing oxygenated species and modifying existing nitrogen functional groups with half-lives on the order of 0.3–17 days (Neish *et al.,* 2008, 2009). Similar experiments demonstrated the presence of the amino acids glycine, aspartic acid, alanine, asparagine, glutamic acid, glutamine, and serine after several months of hydrolysis of Titan-like tholins in ammonia-water solutions (Neish *et al.,* 2010; Cleaves *et al.,* 2014). The net result of these and related experiments argues, as Cleaves *et al.* (2014) pointed out, that regardless of the degree of hydration, mixtures of amino acids and other complex organic molecules can be produced in aqueous tholin solutions in a variety of environments.

Molecules created by the energetic processing of hydrocarbons and other constituents both in gases and in ices can consist of single and multiple aromatic units linked by aliphatic branching structures, and astronomical observations have detected such hydrocarbons in the interstellar medium (Sandford *et al.,* 1991; Pendleton *et al.,* 1994). Laboratory experiments producing organic refractory materials from astrophysically relevant starting components have provided a foundation for understanding the origin and evolution of organic molecules that form on interstellar grains. These materials contribute to the initial inventory of the solar nebula. Solar System objects have revealed the presence of complex organics in both atmospheric and surface compositions, and laboratory studies of tholins have contributed to the understanding of these environments. As with the astrophysically relevant products, the molecular masses of the components of a tholin may reach several hundred or even thousands of daltons. Starting molecules typically include small hydrocarbons, but the carbon source can also be carbon oxides (CO, CO_2, etc., Imanaka *et al.,* 2014), and other initial components can include N_2, NH_3, CH_3OH, and H_2O, for example.

Tholins acquire visible color, typically yellow, orange, red, and brown, during their production, as more π electrons are delocalized in conjugated aliphatic chains and in aromatic rings as these structures grow. Prolonged energetic processing of a colored tholin usually results in a progressive change in color to black, indicating the increasing removal of hydrogen (and oxygen, where relevant), leaving elemental unstructured carbon or graphitic sheets as an ash (*e.g.,* Thompson *et al.,* 1987; Brunetto *et al.,* 2006). Imanaka *et al.* (2004) found that the relative amounts of aromatic and aliphatic components in a gas-phase Titan-mixture of N_2 and CH_4 were dependent on the pressure of the gas during photolysis. Higher pressures lead to higher abundances of aliphatics, while lower pressures yield greater degrees of N-incorporation both in the aliphatic chains and in the aromatic structures. Imanaka's experiments also showed that at low pressures the tholin produced was a darker red in color in comparison with high-pressure tholins, which were yellow.

Pluto's history of the interaction of the surface volatiles with the atmosphere may have resulted in stratified deposits of ices and tholins. If a surface deposit of atmospheric tholin is permeable to underlying volatile ices that could sublime during times of higher local temperature (induced in part by the lower albedo of the tholin), the vapor would be released to the atmosphere, where it would be available for subsequent recondensation on the surface and over time create stratigraphically layered deposits of tholins and ices. Dark strata seen in the tilted ice blocks in the al Idrisi Montes, in the walls of some fossae, and in the walls of old craters in Venera Terra may be due in whole or in part to such cycles (Moore *et al.,* 2016).

3. Tholins in the Context of Pluto's Surface and Geology

In addition to atmospheric tholins, similar refractory organic solids are also produced by the photolysis and radiolysis of ices containing sources of carbon (Khare *et al.,* 1993; McDonald *et al.,* 1996), and this early work has led to new experiments (Materese *et al.,* 2014, 2015) relevant to the discussion here. The work reported here supports the presence of refractory organic solids on the surface of Pluto and shows that their formation and chemical evolution in a geological context may produce a great variety of complex molecules, including the five biological nucleobases. Thus, with evidence from the laboratory, we carry the discussion of prebiotic molecules beyond the formation of amino acids by the hydrolysis of tholins to a higher level of complexity and biological relevance.

Like tholins produced in the laboratory in connection with Solar System problems, astrophysical residues can display color (*e.g.,* Greenberg and Mendoza-Gómez, 1993; Bernstein *et al.,* 1995), and have a great variety of organic functional groups in their final makeup, depending on the starting materials, temperature, photolyzing flux, and so on (Allamandola *et al.,* 1988; Strazzulla and Baratta, 1992; Greenberg *et al.,* 2000; Moore *et al.,* 2001). A comparison of Solar System and astrophysical organics gives insight into the physical and chemical conditions in the interstellar medium and protostellar regions. Tholins made from materials and processes related to planetary atmospheres and surfaces show significant similarities in composition and optical properties to some astrophysical refractory residues, illustrating the wide-spread and ubiquitous nature of complex organic materials in a variety of astronomical settings.

An outstanding question concerning primitive bodies in the Solar System is whether they contain unaltered interstellar material or are composed of material processed in the solar nebula. While there is evidence of the latter through studies of oxygen isotopes (Tartèse *et al.,* 2018) and other lines of study (Ciesla and Sandford, 2012), there are also compelling arguments for the former (Alexander *et al.,* 2017; Altwegg *et al.,* 2017). Studies such as reported here shed additional light on this question through the first detection of complex organics on a small body in the outermost regions of the Solar System that remains close to its place of origin.

Pluto's surface is largely covered with ices of at least five different molecules: N_2, CH_4, CO, H_2O, and C_2H_6, all of which have been detected spectroscopically (Cruikshank *et al.,* 2015). In the solid phase, N_2 and CH_4 occur as a solid solution with proportions at saturation that depend strongly on the temperature, although saturation is not necessary for thermodynamic equilibrium. At Pluto's surface temperature of ~ 40 K, two distinct combinations occur: one which is N_2-rich in which the CH_4 saturation limit is ~ 0.06 (*i.e.,* N_2:CH_4 = 94:6), and another CH_4-rich component in which the N_2 saturation limit is ~ 0.035 (*i.e.,* N_2:CH_4 = 3.5:96.5) (Protopapa *et al.,* 2015, 2017; Schmitt *et al.,* 2017). Although the saturated combinations are not seen on Pluto, both N_2-rich and CH_4-rich components are present; thus the basic materials are available for the formation of tholins with an arbitrarily large N content. In addition, C.M. Dalle Ore *et al.* (personal communication) have detected NH_3 (or possibly $NH_3 \bullet nH_2O$ or an ammonium salt) in association with an exposure of H_2O ice in the vicinity of a tectonic structure (see below), suggesting that ammonia has been a significant contributor to Pluto's chemical evolution.

In connection with the chemistry of Pluto's surface, a few papers have reported results of UV and charged-particle irradiation of a Pluto-relevant mixture of ices consisting of the two most abundant components N_2 and CH_4 in the proportions 100:1, co-deposited on a cold surface in the laboratory. Wu *et al.* (2012) irradiated this mixture at 20 K with UV and reported finding N_3, C_nN (n = 1–3), CN_2, $(CN)_2$, HCN_2, HC_2N, $C(NH)_2$, HN_3, HNC, HCN, $HCCNH^+$, and $NCCN^+$. In similar experiments by Kim and Kaiser (2012), but with addition of CO, a number of additional molecules were observed, including HCO, HNCO, CH_2N_2, CH_3CHO, C_2H_6, and H_2CO. Moore and Hudson (2003) identified a number of molecules and radicals in a N_2-rich ice containing CH_4 and CO irradiated with protons, noting that some observed radicals, such as OCN^-, CN^-, and N_3^- should be stable in the colder regions of Pluto's surface. Many of the products they found are relevant to the synthesis of biomolecules.

Whereas the Wu *et al.* (2012) and the Kim and Kaiser (2012) experiments did not report the production of a refractory residue, comparable experiments by Materese *et al.* (2014) with only *UV irradiation* of an ice of N_2:CH_4:CO (100:1:1), in addition to volatile molecules and radicals stable at low temperature, yielded a yellow-colored component that was visible while the irradiated sample was held at low temperature. In each of the Materese *et al.* experiments, the cycle of deposition of the ice film and irradiation yielded a colored refractory residue which was then harvested at room temperature. Analysis of the residue by several techniques demonstrated the presence of various carboxylic acids, urea, and nitriles, as well as components of high mass (hundreds of daltons). Radicals presumed to have been present in the low-temperature phase of the process as the ice was being irradiated, reacted as the temperature was raised a few tens of degrees on the way to bringing the sample to room temperature (see Greenberg, 1976).

In laboratory experiments using *low-energy electrons* as the energy source for irradiating a mixture of N_2 and CH_4, Wu *et al.* (2013) detected a range of radicals and neutrals similar to those produced by UV photolysis, including N_3, C_nN ($n = 1$–3), CN_2, $(CN)_2$, CH_3N, HCN_2, HC_2N, $C(NH)_2$, HNC, HCN, CH_3, C_2H, C_2H_2, CN^-, NH_3^+, and HC_3N^+. Materese *et al.* (2015) used 1.2 keV electrons to irradiate a Pluto ice mixture with N_2:CH_4:CO (100:1:1), yielding a red-brown colored refractory residue that when analyzed at room temperature was found to contain urea, carboxylic acids, ketones, aldehydes, amines, amides, and nitriles.

Notable in the Materese *et al.* (2014, 2015) experiments is the degree of incorporation of nitrogen in the refractory residue. The UV photolysis experiments resulted in N/C $\sim$0.4 and O/C $\sim$0.3, while in the electron radiolysis experiments N/C $\sim$0.9 and O/C $\sim$0.2. The greater abundance of nitrogen in the radiolized samples arises in part from the ability of the electrons to break the $N \equiv N$ bond in N_2, while the UV flux is inefficient in this process. Figure 2 shows the notional structure of the Pluto ice tholin produced in the electron-radiolysis, accounting for the relative fractions of N, C, and O atoms and the combination of substituted aromatic rings with aliphatic connecting units.

Baratta *et al.* (2015) conducted similar experiments with an ice mixture of N_2:CH_4:CO (1:1:1) irradiated with 200 keV H^+ ions. The IR spectrum of their brown-colored refractory residue was closely similar to that of the Pluto ice tholins made by Materese *et al.* (2015), showing the same functional groups and attesting to the significant inclusion of nitrogen in the solid material.

While many of the molecular species observed in the laboratory at low temperature under energetic irradiation of UV photons are highly reactive, HCN is of special note, as it appears to form both in Pluto's atmosphere and on the surface (Lellouch *et al.,* 2017). HCN is a gateway molecule that through many reaction pathways leads to the formation of purines, pyrimidines, porphyrins, amino acids, and so on (*e.g.,* Ferris *et al.,* 1978; Basile *et al.,* 1984; Borquez *et al.,* 2005; Matthews and Minard, 2008), all of which are of prebiological significance.

On Pluto's surface, the colored materials cover a variety of geological structures of widely differing ages demonstrated by the cratering record (Singer *et al.,* 2016; Robbins *et al.,* 2017). Some colored surfaces also have CH_4, N_2, CO, or H_2O ices in various combinations, but some regions (*e.g.,* Cthulhu) are largely ice-free (Protopapa *et al.,* 2017; Schmitt *et al.,* 2017). Many surface regions studied by New Horizons also include ''banded'' red-white deposits of alternating N_2– and CH_4-rich ice, suggesting seasonal geological processing of surface and near-surface materials (Moore *et al.,* 2016; Howard *et al.,* 2017).

Pluto's surface has regions of different temperatures because of the variety of materials having different albedos and thermal properties, and these temperatures vary with latitude, time of day, and season (Binzel *et al.,* 2017; Earle *et al.,* 2017; Bertrand *et al.,* 2018, 2019). In the coldest regions at $T = 35$–40 K some radicals produced by photolysis of the native materials may be stable, depending on their rates of production and destruction by diffusion and reaction. Thus, the refractory tholin residue at room temperature in the Materese *et al.* (2014, 2015) studies appears to account for some of the colors (Spencer *et al.,* 2016; Olkin *et al.,* 2017; Grundy *et al.,* 2018), although it does not necessarily represent the total molecular inventory on the planet.

4. Prebiotic Chemistry on Pluto's Surface

Tholins generated from laboratory experiments involving the radiation processing of ices relevant to the surface of Pluto are highly complex, partly insoluble organic mixtures. As previously stated, spectral data including infrared (IR) and X-ray near edge structure (XANES) indicate the presence

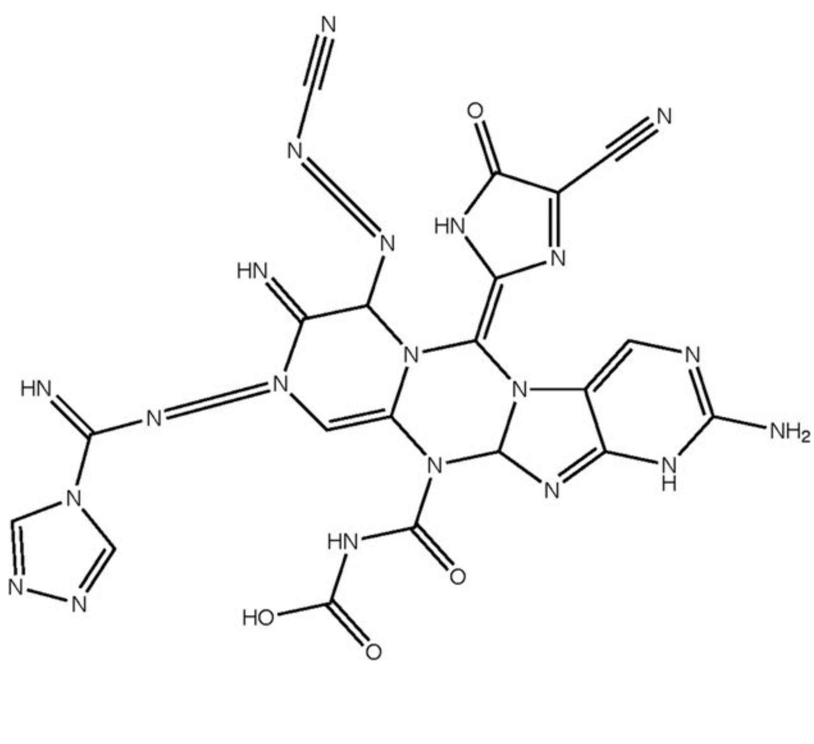

FIG. 2. Notional structure of Pluto ice tholin (Materese *et al.,* 2015). This diagram accounts for the observed N/C and O/C atoms in the tholin produced by the 1.2 keV e^- radiolysis of an ice mixture of $N_2 + CH_4 + CO$ (100:1:1), and the high degree of aromaticity determined from UV fluorescence and mass spectroscopy (Cruikshank *et al.,* 2016). Other ring structures equivalent to pyramidine and purine, while not directly observed, are plausible alternative structures.

of amines, ketones, amides, and nitriles; numerous small carboxylic acids and urea were also identified as part of the tholins in the experiments of Materese *et al.* (2014, 2015) (Fig. 2). While some of these compounds are of prebiotic interest in their own right, several components of the complex organic material in these tholins have the potential to undergo aqueous chemistry to yield molecules of prebiotic relevance. Notably, tholins from ices processed by 1.2 keV electrons consisted of highly unsaturated molecules and many aromatic structures, and a high degree of nitrogen incorporation (N/C $\sim$0.9). If introduced to an aqueous environment, especially an ammoniated solution, such tholins are likely to be modified by hydrolysis to yield heterocycles and peptides, as observed in the experiments by Khare *et al.* (1986), Neish *et al.* (2010), and Cleaves *et al.* (2014), which have the potential to expand greatly the catalog of compounds of prebiotic interest.

Although the hydrolysis of Pluto ice tholins has not yet been studied experimentally, some general insight can be gained from hydrolysis experiments involving similar materials. These not only include atmospheric tholins but also polymerized hydrogen cyanide (poly-HCN). While far from a perfect analog, there are numerous similarities between Pluto ice tholins and poly-HCN. Notably, both are complex mixtures of highly unsaturated molecules with a high degree of nitrogen incorporation. Spectral analyses of these mixtures suggest that they both possess similar functional groups, although ice tholins appear to be more chemically complex than poly-HCN (Materese *et al.,* 2015). Since the early 1960s it has been known that introducing poly-HCN to water rapidly yields solutions with detectable levels of amino acids and nucleobases (Oró, 1961; Oró and Kamat, 1961; Oró and Kimball, 1961). Despite the heterogeneity of poly-HCN, this hydrolysis chemistry appears remarkably robust and yields these compounds, including ketyl and acetyl groups, irrespective of how the polymer was initially generated (Matthews and Minard, 2008). The variety and overall abundances of amino acids and nucleobases produced by these hydrolysis experiments were shown to increase when introduced to acidic or basic conditions. One series of experiments involving HCN-polymers generated from a dilute solution of NH_4CN frozen at -78°C for 27 years yielded adenine, guanine, uracil, and eight other nonbiological nucleobases after hydrolysis (Miyakawa *et al.,* 2002). This study underscored the importance of hydrolysis to the detection of molecules of prebiotic interest because seven of the pyrimidines and purines observed in the hydrolyzed samples were not detected in nonhydrolyzed samples.

We note that pyrimidines, purines, and some nucleobases (including uracil) are found in some meteorites (*e.g.,* Sephton, 2002; Pizzarello *et al.,* 2006). Martins *et al.* 2008 and others have demonstrated through isotopic analysis that the nucleobases in the Murchison meteorite are extraterrestrial in origin. Noting that these molecules would form very slowly and then could be easily destroyed on interstellar dust grains, they conclude that the meteorite nucleobases are instead synthesized by aqueous processes on the meteorite parent body. Because some nucleobases are degraded in an aqueous environment, the final distribution of the individual molecular species ultimately depends on the balance between synthesis and degradation. Recent laboratory work (Modica *et al.* 2018) supports the view that an important source of amino acids in the early Solar System arises from photo- and thermo-processing of icy grains prior to accretion in planetary bodies.

No nucleobases or amino acids were directly identified in analyses of laboratory analogs of Pluto ice tholins (Materese *et al.,* 2014, 2015). However, these samples were analyzed by gas chromatography–mass spectroscopy as quickly as possible after extraction from the vacuum chamber and were never introduced to aqueous conditions. Pluto ice tholins may experience similar hydrolysis chemistry to that which has been observed for Titan atmospheric tholins and poly-HCN. If this is the case, then it is reasonable to suspect that if ice tholins produced near the surface of Pluto are introduced to a subsurface reservoir of liquid water through a resurfacing event, then nucleobases and amino acids may be among the resulting products. We posit that on Pluto, as on Earth, the formation of prebiotic molecules requires the presence of abundant water molecules.

5. Water Ice and Ammonia

Water ice is exposed on Pluto's surface in limited but significant geographical and geological surface units (Cook *et al.,* 2016, 2019; Protopapa *et al.,* 2017; Schmitt *et al.,* 2017) (Fig. 3). Water ice has an exceedingly low vapor pressure at Pluto's temperature and is regarded as bedrock that underlies the more volatile components (N_2, CH_4, CO, and other molecules). In some locations H_2O ice is exposed in the absence of those molecules and sometimes in association with one or more of them. Water ice as bedrock is exposed only where there is no thick overcoat of the volatile ices and where the tholin cover is thin (Cook *et al.,* 2016, 2019; Schmitt *et al.,* 2017; Protopapa *et al.,* 2017).

A large exposure of H_2O ice in association with dark colored tholin deposits and minimal volatile ices is found in Cthulhu, which occupies a wide band along Pluto's equator and incorporates a number of geological structures that include large craters, mountain ranges, and tectonic troughs, that is, fossae (Moore *et al.,* 2016). An especially prominent and interesting trough, Virgil Fossae, which is identified as a graben, has a nearly smooth floor that exhibits an exposure of H_2O ice and a unique color (Fig. 4), first noted by A.H. Parker (personal communication) and Olkin *et al.* (2017). The association of colored material with the fossae also occurs in a radiating graben cluster provisionally named Mwindo Fossae (Fig. 5) that includes Sleipnir Fossa, centered in eroded, undulating uplands near 30°N and 245°E (Moore *et al.,* 2016, their Fig. 2). In this case, the red material lies in the graben, as it does in Virgil Fossae, and there is a clear signature of H_2O ice that is spatially well correlated with the red color (Fig. 5a, 5b).

Although not considered further in this paper, an exposure of H_2O ice (tentatively called Supay Facula) is associated with a well-defined crater (Pulfrich Crater at $\sim$29°N and 215°E) and in surrounding patches of the terrain. Moderate coloring of the icy patches and Pulfrich itself occurs, but these are not as prominent as in Virgil Fossae, nor is the color significantly different from some of the regions elsewhere on the planet.

Three plausible scenarios for the appearance of exposures of H_2O ice on Pluto's surface emerge. One possibility is the

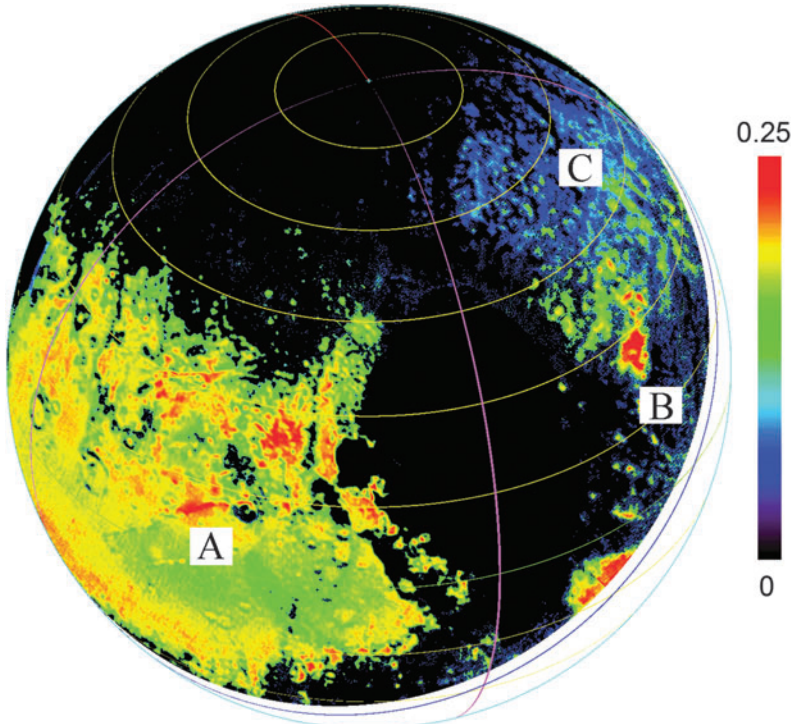

FIG. 3. The distribution of H_2O ice on Pluto's surface. Colors indicate increased concentration of the ice, with regions having strongest H_2O ice bands shown in red. The region marked (A) corresponds to Virgil Fossae (see Fig. 4), (B) is the Pulfrich Crater region, and (C) is the region of Mwinido Fossae and Sleipnir Fossa (see Fig. 5). After Schmitt *et al.* (2017, Fig. 28C).

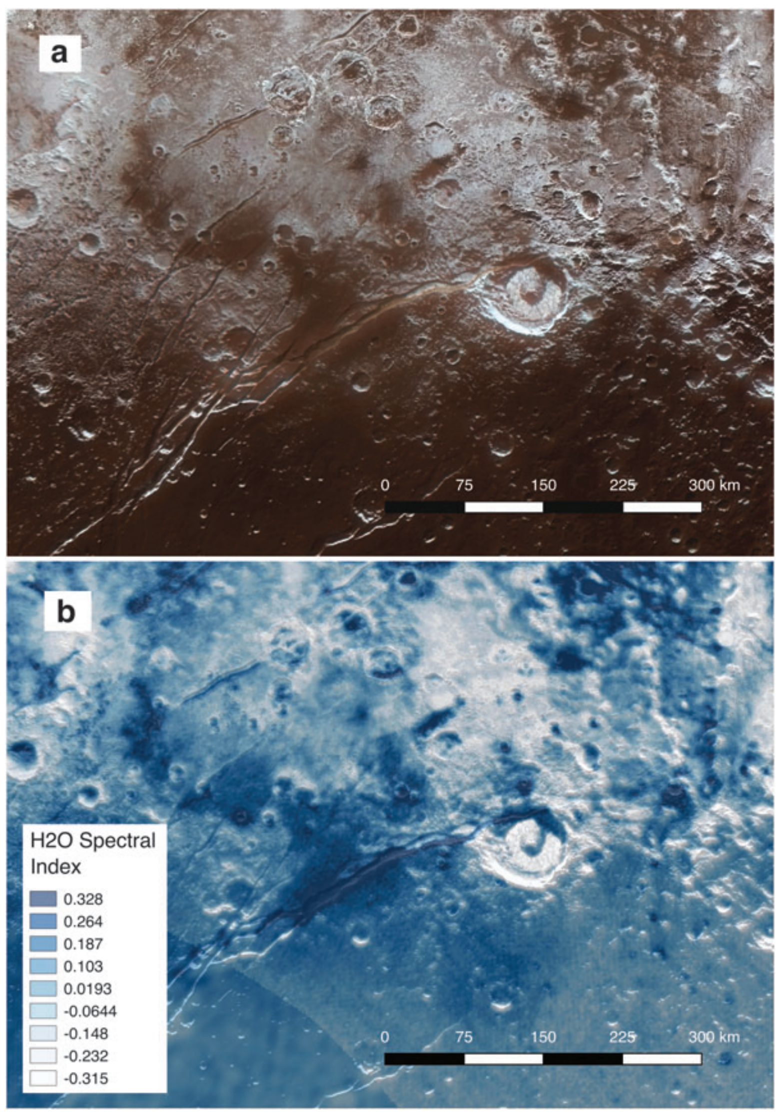

FIG. 4. (**a**) Red coloration and water ice exposures in and around Virgil Fossae, which lies on the northern edge of Cthulhu. The large crater is Elliot Crater. (**b**) The darkest blue color represents the strongest H_2O concentration centered on Virgil Fossae, with lesser concentrations at distances somewhat more than 100 km from the main concentration. Virgil Fossae is a graben formed by parallel extensional normal faults (Keane *et al.,* 2016; Moore *et al.,* 2016). Fractures surrounding the damage zones of faults can increase the permeability of the host rock, resulting in greater mobility of subsurface fluids (Caine *et al.,* 1996). The rhomb-shaped tectonic region to the west (left) is likely associated with a deep fracture network, potentially enabling subsurface fluid transport to the surface (Davatzes *et al.,* 2005). Top frame is from NASA PIA19952. The two frames have slightly different map projections.

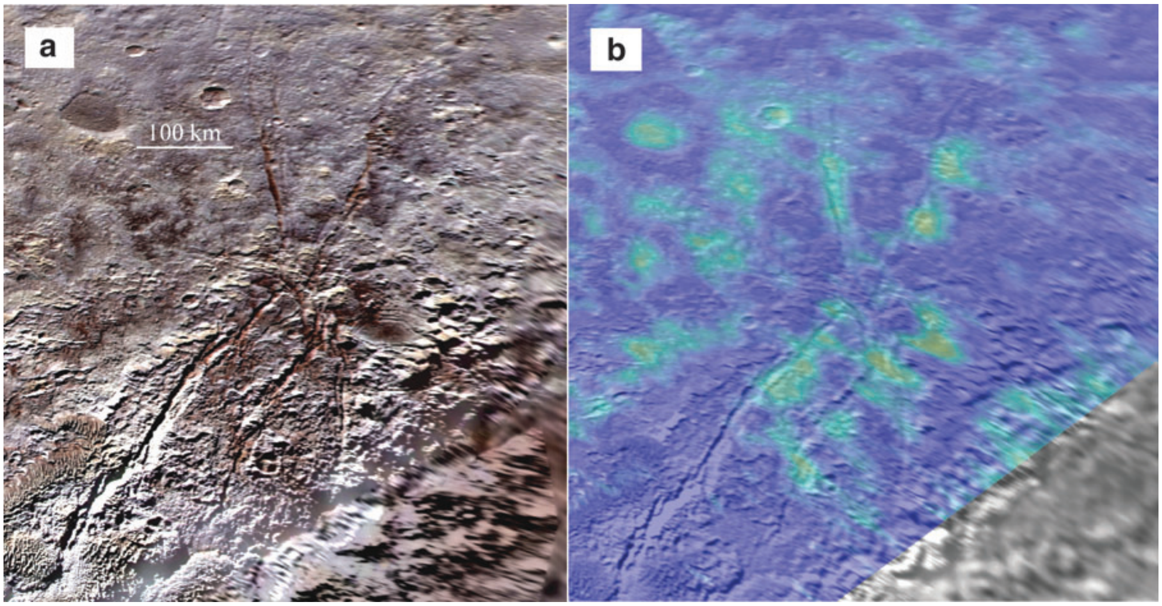

FIG. 5. (**a**) Red material exposed in a radiating graben system tentatively designated Mwindo Fossae. (**b**) Distribution of H_2O ice from the map by Schmitt *et al.* (2017); the strongest H_2O ice abundance is colored yellow, and less abundance is green. The H_2O overlay map is based on New Horizons LEISA data, which have lower spatial resolution than the basemap made from the MVIC instrument. On Earth and Mars, radiating graben are often associated with magmatic dike swarms at depth and possible subsurface fluid expulsion (Mastin and Pollard, 1988; Head *et al.,* 2003; Davatzes *et al.,* 2005; Runyon, 2011).

exhumation of the H_2O ice bedrock by the removal of the more volatile and seasonally deposited ices over limited geographical regions, producing a type of vapor-driven lag deposit. In this case, the most likely reason for exposing the bedrock is the failure of N_2, CH_4, and CO to condense onto a surface that is too warm for their retention, such warming as could arise from the lower albedo of that region. A second possibility is the glacial scouring by more volatile ices overlying the water ice bedrock by one or more geomorphological mechanisms (Howard *et al.,* 2017). The third scenario involves ejection of liquid or a slurry of H_2O from the subsurface onto the visible surface (i.e., cryovolcanism), where it quickly freezes solid. Once frozen, the exceedingly low vapor pressure of the mixed solid would preserve it indefinitely.

For the ejection of liquid H_2O from the interior, at least two conditions must be met: H_2O in the subsurface must exist as a liquid or a slurry, at least episodically, and there must be a plausible mechanism for its break-through to the surface. In an analysis of spectral images of the H_2O ice exposure at Virgil Fossae, C.M. Dalle Ore *et al.* (personal communication) have identified the spectral signature of ammonia, most likely occurring as a hydrate in the H_2O, but possibly as an ammoniated salt. Ammonia in solution with liquid water reduces the freezing temperature by as much as 100 K, while increasing the viscosity of the mixture (Kargel *et al.,* 1991), and at the same time promotes the formation of ammonia hydrates, such as $2NH_3{\bullet}H_2O$, $NH_3{\bullet}H_2O$, and $NH_3{\bullet}2H_2O$ (Delzeit *et al.,* 1997; Uras and Devlin, 2000; Uras *et al.,* 2000). Circumstantial evidence for a significant liquid H_2O ice region of the upper mantle of Pluto, at least at some time in the past, comes from an analysis of the orientation of the planet and its moon Charon. Charon is locked in synchronous rotation/revolution on a line antipodal to Pluto's Sputnik Planitia, a frozen, slowly convecting nitrogen ''sea'' having a depth of a few kilometers. Nimmo *et al.* (2017) showed that Pluto is so roundly spherical and in apparent hydrostatic equilibrium that it must have contained a liquid interior when first formed and while Charon was close to the planet after formation. Nimmo *et al.* (2016) made the case that a positive gravity anomaly under the basin that now contains the frozen nitrogen sea could have acted to orient Pluto and Charon in their present configuration, while Keane *et al.* (2016) proposed that the mass loading of the basin by the nitrogen layer could also create a reorienting gravity anomaly. Such a gravity anomaly would arise if the solid crust above a liquid water mantle were thinned by a large-scale impact that created the basin in which the nitrogen later condensed and accumulated on the surface to form what we now see as Sputnik Planitia.

Regarding a mechanism for the ejection of liquid H_2O from a subsurface ocean to the surface, Neveu *et al.* (2015) demonstrated through geochemical modeling and other considerations that gas generated in the interior of Pluto (and some other Kuiper Belt objects) through rock-liquid interactions could propel liquid water through cracks in the icy crust and eject the fluid explosively on the surface. In the specific case of Pluto, Neveu *et al.* (2015) regarded CO as the most likely gas to charge and pressurize a body of subsurface liquid H_2O, with the expectation that tectonically fractured surface regions would provide ready access of liquid to the surface. Regions of the crust fractured by an impact (*e.g.,* Pulfrich Crater) and tectonic faulting, forming graben (*e.g.,* Virgil Fossae), could provide this pathway. Although NH_3 in H_2O reduces the freezing temperature of the mixture, liquid H_2O-NH_3 emerging onto the surface will quickly freeze. Rapid exsolution of dissolved gases in the vacuum of the surface environment will chill the surface of a flow, termed a cryolava, to form a solid crust with liquid below. At the same time, the bottom layer of the flow will freeze from contacting the ground rock at $T \sim 40$ K. During this rapidly evolving process, some material on the native surface may be incorporated into the cryolava and possibly dissolved in it before freezing. The physics of such a cryolava flow emerging on Pluto's surface can be modeled by using laboratory data on H_2O-NH_3 fluids and with several assumptions, but is beyond the scope of this paper.

Some of the water-ice-rich regions on Pluto are strongly tinted with tholins, but some are not. Differences in color may represent either a chemical difference or the way in which the material is entrained in a transparent ice. Here we consider the unique chemistry of tholins that may form in the liquid water in Pluto's interior and are ejected to the surface together as a mixture. As a historical note, we point out that in the original Miller-Urey experiments with the synthesis of amino acids in a mixture of H_2O vapor and gaseous CH_4, H_2, and NH_3 exposed to high-voltage sparks (Miller 1953), the condensed liquid in which the amino acids were found was colored. Miller attributed the color, which ranged from pink to deep red over the course of the exposure of the mixture to the spark, as well as yellow solid material, to organic compounds adsorbed on bits of colloidal silica leached from the glass apparatus and suspended in the liquid. Some of Miller's sealed preserved samples from the original and subsequent experiments, all strongly colored, were analyzed many years later with modern sensitive techniques by Johnson *et al.* (2008) and were found to contain several more amino acids than Miller found. More details of the history of this development and how it led to the study of colored organic residues in astronomical objects are found in Cruikshank and Sheehan (2018).

In the broader context of the chemistry of the Solar System, we note that formaldehyde (CH_2O) found in interstellar ices was incorporated into the early solar nebula. The role of formaldehyde polymer in the formation of complex organic matter in Solar System bodies has been explored in the laboratory to understand the chemistry of the insoluble organic matter in meteorites and refractory organic carbon in comets by studying polymerization reactions at different temperatures and in the presence of ammonia (Cody *et al.,* 2011; Kebukawa *et al.,* 2013). Using a solution of formaldehyde, glycoaldehyde, and ammonia, Kebukawa *et al.* (2017) showed that a suite of complex amino acids could be synthesized simultaneously with insoluble organic matter in hydrothermal experiments simulating processing in aqueous environments in planetesimals. Sekine *et al.* (2017) also conducted laboratory experiments with formaldehyde, glycoaldehyde, and ammonia in solution, finding that with prolonged heating of the liquid, a dark refractory residue formed. The high-molecular-weight material consisted of formaldehyde polymer, as well as olefinic and aromatic molecules. They extended the laboratory results to suggest that the dark reddish regions on Pluto may have originated from material produced in the heating of Pluto's native materials, which are presumed to have included both formaldehyde and ammonia, by the giant impact that is considered a likely cause of the formation of Charon (Canup, 2005). As noted above, C.M. Dalle Ore *et al.* (personal communication) detected NH_3 in the apron of H_2O ice and red tholin surrounding Virgil Fossae.

Because of the highly correlated colocation of the H_2O ice and the uniquely red tholin that covers the floor of Virgil Fossae, we posit that this material came to the surface as a liquid along the fault scarps that define the main fossa (a graben). As noted, the Virgil deposit is distinguished from other tholins by its color in the visible spectral region (Spencer *et al.*, 2016), suggesting a source that is different from tholins made by atmospheric photolysis or by radiation processing of surface ices. The difference in color comparisons between the Virgil tholin and those on the adjacent and more distant surface regions may indicate different tholin compositions; nonetheless, the idea presented here that the Virgil tholin came to the surface mixed with liquid H_2O-NH_3 is plausible from both a geological and a chemical point of view. Formation of a liquid with an organic chromophore would appear to require sources of carbon (*e.g.,* CH_4 and other hydrocarbons) and nitrogen (*e.g.,* N_2 and NH_3), in addition to energy (*e.g.,* thermal) to cause the reactions resulting in this particular variety of tholin. Thermal energy sufficient to drive chemical reactions may have come from the relatively hot liquid water erupting from a subsurface reservoir onto the cold surface of Pluto. In considering the origin and stability of the spectral signature of ammonia (or ammonia hydrate or ammonium salt) in Virgil Fossae and surroundings, C.M. Dalle Ore *et al.* (personal communication) concluded from the presence of NH_3, H_2O, and the uniquely colored tholin together, that the material was likely ejected from a subsurface source, probably no earlier than $\sim 10^9$ y ago.

Figure 6 summarizes the sources of colored, complex organic tholins that occur on Pluto's surface, including the subsurface source proposed here to account for the distribution of tholin and NH_3-enriched H_2O ice.

Although in this paper we advance the view that tholin is the chromophore in the ice in and around Virgil Fossae, Kargel (1992) notes that sulfur- and carbon-bearing constituents dissolved in ammoniated water would, when photolyzed on an exposed surface, produce chromophores. At the same time, Kebukawa *et al.* (2017) made the case that the variety of organic matter found in aqueously altered carbonaceous meteorites can be produced by the many reactions of formaldehyde, glycoaldehyde, and ammonia in various basic and acidic aqueous environments that are plausible in planetesimals in different regions of the early Solar System, or perhaps in a single large planetesimal such as Pluto. In this view, the formation of different suites of complex organics with different chromophores in hydrothermal environments inside Pluto and ejected onto the surface at various times in different locations might account for some of the variety of colors now evident. In the absence of specific data on this point, we do not consider this possibility further.

6. Physical and Chemical Properties of the Uniquely Red Tholin in Virgil Fossae

The uniquely red-colored tholin and its correlation with H_2O ice in Virgil Fossae and a few surrounding regions might be explained by the mixed model calculations of Grundy (2009). Grundy considered three models having the same composition for a transparent ice containing a dispersion of subwavelength-sized red particles but different mean optical pathlengths in the surface exposed to sunlight and the observer. An exposure of ice with entrained particles and having a fine-grained surface texture has a small

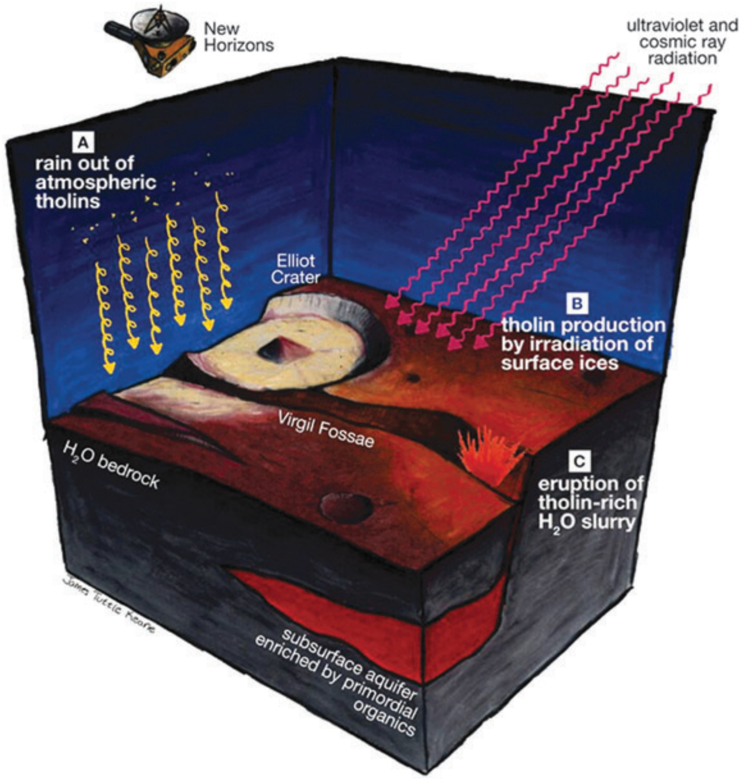

FIG. 6. Three sources of tholins on Pluto's surface. Tholins from photochemistry in the atmosphere are initially yellow, as seen on the young surface of Sputnik Planitia (see Fig. 1), while surface ices processed by UV and charged particles have darker colors ranging from red to brown. Material having the uniquely red color in Virgil Fossae and surrounding landscape appears to have come from subsurface sources through cryovolcanic processes. Graphic by J.T. Keane.

mean optical path, (l_{MOPL}). Under these conditions, incident sunlight is efficiently scattered back to space with little penetration into the ice and the surface, resulting in a colorless surface. In the case when l_{MOPL} is very large, representing a much smoother and coarser grained surface texture, sunlight is absorbed at all wavelengths at which the particles and the medium absorb, and the surface will appear very dark (*i.e.,* the material is thick enough to be ''optically thick'' and an efficient absorber at all wavelengths). In Grundy's models, an intermediate case between the two extremes can reveal a colorful spectral reflectance, depending on the intrinsic color of the entrained particles (the variation of the absorption coefficient with wavelength). His calculations incorporated Maxwell-Garnett theory for the mixing of two materials with different absorption coefficients representing the medium and entrained colored particles having dimensions less than the wavelength of the light in the spectral region relevant to the appearance of the color.

Considering the color and coincidence of tholin material with H_2O ice in and around Virgil Fossae, if extremely small particles of red-colored tholins are mixed in the ice, the color presently observed may be close to the intrinsic color of the tholin, and the surface has a texture that is represented by Grundy's intermediate l_{MOPL} case. Grundy notes that the volume concentration of entrained colored particles also affects the color and albedo of the mixture and that removal of the ice will lower albedo and flatten the color curve to make a black or near-black surface (another instance of a system becoming ''optically thick'' and dark). In the case of Pluto, loss of the H_2O ice would likely occur through some erosional mechanism operating at a micro scale rather than sublimation, since the vapor pressure of H_2O ice at Pluto's surface temperature is extremely low and water ice is stable on geological timescales.

The implications of applying Grundy's calculations to the color of Virgil Fossae and its nearby regions are significant in terms of the composition, particle sizes, and dispersion of complex organic solids in association with H_2O ice and the subsequent chemistry as the mixture is exposed to UV or other sources of energy. Although unlikely, it is possible to imagine a scenario in which H_2O-NH_3 is ejected from Pluto's subsurface, perhaps in the manner described and modeled by Neveu *et al.* (2015), and then mixed with a preexisting tholin-rich surface layer to yield the presently observed geographical distribution of both H_2O ice and coloration. As noted above, some preexisting surface material may have been incorporated into the flowing cryolava before it froze. However, an alternative scenario is the following:

Liquid ammonia-bearing water reaching the surface of Pluto was transporting an insoluble fraction of colored particles of complex organics akin to tholins that were already present in the subsurface reservoir, and the liquid was ejected onto the planet's surface under pressure. Some tholin-bearing liquid emerged along the fractures defining existing branches of the fossa complex, flowing short distances ($\sim$1–3 km) before freezing solid. The main exposure is in the fossa floor $\sim$200 km west of Elliot Crater, while some of the fluid reached the surface in the portion of the graben crossing the north rim of Elliot. From one or more vents along the fossa, a substantial quantity of the freezing fluid was sprayed on the high walls of Virgil and onto the surrounding terrain, reaching a distance >100 km in some directions. Tholin-laden water ice probably also emerged through a number of additional vents, several of which were associated with medium-sized craters and their surroundings north and east of the main channel of the fossa where the unique red color is also evident. Modeling of the physics of the flow of this cryolava is in progress to explore details of flow thickness, viscosity, and other parameters (O.M. Umurhan, personal communication).

The scenario in which complex organic material is mixed with liquid water in Pluto's subsurface carries important implications for the chemistry occurring in that environment, including but not limited to the formation of amino acids. Organic complexes containing the basic structural elements of pyrimidines and purines in combinations of H_2O and NH_3 ice, when photolyzed with UV light, readily produce additional complex products including a number of nucleobases, as demonstrated in the laboratory (Nuevo *et al.,* 2009, 2012, 2014; Materese *et al.,* 2013, 2017). Among the nucleobases identified in the photolyzed mixture are adenine, guanine, uracil, cytosine, and thymine. We discuss this in detail below.

If some of Pluto's tholin now seen on the surface at Virgil Fossae is present in the interior, it may have originated in the Charon-forming impact event scenario described by Sekine *et al.* (2017) discussed above (see also Simonelli and Reynolds, 1989), or perhaps synthesized later *in situ* in a chemical environment similar in some respects to that in the original experiments by Miller (1953), in which a red liquid resulted from the deposition of energy in a reducing mixture of gases and H_2O vapor and then buried in the subsurface. If, instead, the red material were an original component of Pluto, the implications for its occurrence as part of the feedstock from which Pluto and other small bodies in the outer Solar System formed bear on the even larger question of the origin of this material in the solar nebula or in the interstellar medium mentioned above (also Simonelli and Reynolds, 1989). Pluto has been revealed by New Horizons to be a geologically and chemically dynamic body, but its methane, nitrogen, water, and carbon monoxide have not been processed completely into more complex materials; thus the planet clearly retains some primitive aspects of its initial components.

7. Nucleobases from Pyrimidine and Purine in H_2O Ice

The following discussion frames the picture of Pluto's organic tholins and ices in the context of laboratory synthesis of complex molecules of greater prebiological importance than has previously been recognized. Specifically, we posit that nucleobases, including those of biological significance, may have formed in tholins embedded in the H_2O-NH_3 ice on the surface or in a liquid water interior reservoir and then carried to the surface and deposited in and around Virgil Fossae and perhaps other regions on Pluto's surface.

All naturally occurring terrestrial biologically derived nucleobases are derivatives of the N-heterocycles pyrimidine or purine. Extensive work conducted in the NASA Ames Astrochemistry Laboratory has demonstrated that all the biological nucleobases and other nonbiological isomers are readily produced by the radiation processing of pyrimidine and purine in various water-dominated ice mixtures (Nuevo *et al.,* 2009, 2012, 2014; Materese *et al.,* 2013, 2017; Sandford *et al.* 2014). In the Materese *et al.* (2017) experiments, the (pyrimidine + H_2O ice) and the (purine + H_2O ice) mixtures were irradiated with a Lyman-α flux of $\sim 10^{15}$ photons/cm^2/s for 44–48 h, resulting in a total dose of $\sim 1.66 \times 10^{20}$ photons/cm^2. With the total Lyman-α flux at Pluto (solar plus interplanetary medium) of $\sim 3.4 \times 10^8$ photons/s (Gladstone *et al.,* 2018), the laboratory experiments correspond to $\sim 1.6 \times 10^4$ y on the planet if the atmosphere were completely transparent. As noted above, the atmospheric transparency varies temporally with the mixing ratio of CH_4 from $\sim$0.01% to 10% (Bertrand *et al.,* 2019). Scaling the surface exposure time relevant to the laboratory experiments with these transmission values yields a range of $\sim 1.6 \times 10^5$ to 1.6×10^8 y to make the nucleobases of interest.

Experiments show that the water ice matrix plays a vital role in the production of pyrimidine and purine derivatives via ice radiation chemistry (Nuevo *et al.,* 2012; Materese *et al.,* 2013). Quantum chemical modeling of these reactions has shed further light on this process, demonstrating that the water serves as a proton acceptor for the peripheral hydrogen atoms shed by the pyrimidine or purine during the reaction, greatly improving the thermodynamic favorability of this process (Bera *et al.,* 2010). H_3O^+, the hydronium ion, is a well-known low- energy, stable complex in liquid and solid water.

The most chemically simple of the pyrimidine biological nucleobases is uracil (Fig. 7d), whose synthesis from pyrimidine would only require the addition of two oxygen moieties. In an initial attempt to study the production of uracil in an astrophysically relevant ice, simple low-temperature (15 K) binary mixtures of H_2O and pyrimidine ice were irradiated by UV photons (primarily Lyman-α) and then allowed to warm to room temperature for extraction and analysis by gas chromatography coupled with mass spectrometry and high-performance liquid chromatography (Nuevo *et al.,* 2009). Numerous singly and doubly oxygen substituted pyrimidine derivatives, including uracil, were

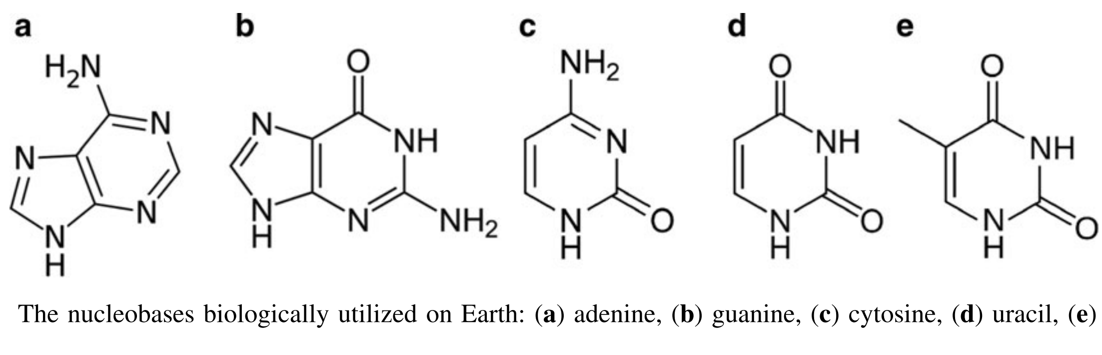

FIG. 7. The nucleobases biologically utilized on Earth: (**a**) adenine, (**b**) guanine, (**c**) cytosine, (**d**) uracil, (**e**) thymine.

readily observed in the refractory residues produced in these experiments. Importantly, singly substituted pyrimidine derivatives were vastly more abundant than doubly substituted variants. This is because multiply substituted variants require multiple photons to produce and because there are more ways that the production of any individual product can be derailed (*e.g.,* a new photon cleaves a previously added side group rather than removing a hydrogen to allow a second substitution).

Production of cytosine (Fig. 7c) from pyrimidine photochemistry requires the addition of an oxygen and one amino functional group. For these experiments, three-component ice mixtures consisting of H_2O, NH_3, and pyrimidine were subjected to UV-radiation processing (Nuevo *et al.,* 2012). These residues were analyzed by using the same techniques as those of Nuevo *et al.* 2009. The results of this work demonstrated that all the oxygenated pyrimidine derivatives that were formed during the experiments ended up in binary H_2O and pyrimidine ice mixtures also formed in these experiments. Additionally, a suite of aminated pyrimidine derivatives was detected in these residues, including the nucleobase cytosine. Relative abundances of singly and doubly substituted derivatives followed the same general pattern as observed for binary H_2O:pyrimidine ices, although more variants were possible because multiply substituted derivatives could involve different functional groups. The presence of ammonia in these ice mixtures enhanced the production yields of uracil and singly substituted oxygen derivatives relative to their observed abundances in binary ice mixtures. Additionally, the most abundant double oxygen–bearing pyrimidine derivative in these experiments was uracil, while the most abundant aminohydroxypyrimidine derivative was cytosine. The effects of NH_3 in the laboratory experiments support the view that the deposits in and around Virgil Fossae are likely to carry inventories of these molecules.

Thymine (Fig. 7e), the least abundant of the nucleobases synthesized from pyrimidine through photochemical processing, requires the addition of two oxygen moieties and a methyl group. To study the formation of thymine, Materese *et al.* (2017) conducted photochemical experiments using ice mixtures containing H_2O, CH_3OH, and pyrimidine (series A) or H_2O, CH_4, and pyrimidine (series B). Experiments in series A yielded the same oxygen-bearing pyrimidines detected in the previous experiments in addition to pyrimidine methanols but no thymine. Experiments in series B also yielded the oxygen-bearing pyrimidines, and a series of methylpyrimidines, and may have contained trace quantities of thymine, but it could not be unambiguously identified. Additional experiments using the series B ice mixture with triple the radiation dosage yielded unambiguous detections of thymine. It was hypothesized that several important factors contribute to the relatively low abundance of thymine compared with the other nucleobases. The most important factor is that thymine formation requires the addition of three functional groups rather than the two required by uracil and cytosine. More functional group additions mean more photons required to drive the process and more potential ways that this synthesis can be derailed by either following a reverse reaction that removes a group that was previously added or by adding a group in a wrong location. Additionally, quantum chemical calculations have demonstrated that methyl group addition is less energetically favorable than hydroxyl- or amino-group addition (Bera *et al.,* 2016). The low abundance of thymine is especially interesting from an astrobiological perspective because uracil and cytosine are required to produce RNA, but thymine is not.

The nucleobases adenine and guanine are both based on the purine ring structure. The formation of adenine requires the addition of a single amino group to purine, while the formation of guanine requires the addition of both an oxygen moiety and an amino group. The production of adenine and the production of guanine were simultaneously studied through the UV photoprocessing of H_2O, NH_3, and purine ice mixtures (Materese *et al.,* 2017). In these experiments, all singly and most doubly substituted purine derivatives bearing either an oxygen moiety or an amino group were likely detected, with some of the identities inferred from their mass spectra. Among the compounds positively identified were adenine and guanine. As was found in experiments involving the formation of the pyrimidic bases, doubly substituted purine derivatives such as guanine were far less abundant than singly substituted purines such as adenine ($\sim$100:1 adenine:guanine). Notably, hypoxanthine, which can serve as a base-paring substitute for guanine (Crick, 1968; Cafferty and Hud, 2015) is the most abundant purine derivative observed in the residues.

Small heterocycles such as purine and pyrimidine may be among the innumerable compounds that make up both atmospheric and ice-derived tholins, as well as tholins formed in possible interior fluid pockets on Pluto (discussed above). Consequently, it is conceivable that nucleobases were able to form on Pluto's surface in locations where these tholins are intermixed with ammoniated water ice.

8. Summary and Conclusions

The main points of this paper are as follows:

(1) Pluto's surface is colored by organic complexes (tholins) largely derived from processed atmospheric gases and surface ices.
(2) One geologically important structure (Virgil Fossae) exhibits an exposure of H_2O-NH_3 ice and a uniquely red color and may contain tholins produced in a subsurface reservoir in addition to tholins from the atmosphere and processed surface ices.
(3) The ice and the coloring agent (a tholin) may have been generated as a fluid mixture that erupted onto the surface with both a flowing liquid and an airborne component.
(4) In the laboratory, tholins made by UV and charged particle irradiation of Pluto-relevant ice mixtures (N_2+CH+CO: 100:1:1) have colors that match several regions on Pluto, and contain aromatic structures similar to purines and pyrimidines. UV photolysis of purines and pyrimidines in an H_2O-NH_3 ice matrix produces nucleobases, including the five that are biologically significant on Earth.
(5) The uniquely red-colored H_2O ice at Virgil Fossae may contain nucleobases and amino acids, although they are not directly detected in available spectroscopic data for the planet owing to the limited capabilities of the near-IR spectrometer on the New Horizons spacecraft.

Pluto's highly varied surface composition consists of a majority of volatile and nonvolatile ices plus an array of minor coloring agents attributed to organic complexes (tholins), all found in a great variety of geological structures. This leads us directly to an investigation of the origin and evolution of the planet in the context of prebiotic organic chemistry. We have presented supporting evidence that the variety of surface colors results from the synthesis of complex organics in Pluto's atmosphere (gas-phase tholins, *e.g.,* Grundy *et al.,* 2018) and on the surface (ice-phase tholins, *e.g.,* Cruikshank *et al.,* 2015), as well as tholins and other organics from the subsurface carried to the surface by ammoniated liquid water to form deposits of unique color and chemical properties. The geological evidence in images of Pluto's surface structures from the New Horizons spacecraft supports the ejection of ammoniated water in one or more fountaining eruptions emanating from a part of Virgil Fossae and carrying this material on ballistic trajectories for about 100 km.

Pluto's organic tholins and ices, when viewed in the context of laboratory syntheses of complex molecules of great prebiological importance, lead to a deeper understanding of the plausible chemistry that may be occurring on icy bodies in the outer Solar System as well as on icy exoplanetary bodies. Nucleobases, including those of known biological significance, may have easily formed from the interaction of nitrogen-rich tholins with warm subsurface water ejected onto the surface in cryovolcanic events and then processed by UV radiation, or these complex molecules may have already been present in subsurface fluid that emerged in and around Virgil Fossae, similar to the mechanism thought to stain the jovian moon Europa's water ejection sites.

In considering some of Pluto's geological structures, we have presented a plausible scenario in which complex organic tholins are embedded in exposures of frozen H_2O on the surface. Guided by recent laboratory experiments with organics in H_2O ice, we consider the additional chemistry that may occur on Pluto's surface. In addition, Pluto may have (or once had) a large-scale subsurface ocean of liquid H_2O (Nimmo *et al.,* 2016), and chemical processes in that ocean or in more limited subsurface reservoirs may have produced tholins that have been carried to the surface by liquid water or other fluids such as liquid N_2 and are now exposed to view. A primordial source of tholin-like material might also have been preserved and incorporated during accretion and be transportable to the surface via a variety of possible mechanisms (Singer *et al.,* 2017). Glacial scouring (Howard *et al.,* 2017), cratering (Singer *et al.,* 2016; Robbins *et al.,* 2017), and other recent or current processes of surface evolution on Pluto may also expose ancient concentrations of organic-rich mantle materials.

Some of the oldest organics might even derive from the material inherited during the formation of the planet. Observations of molecular clouds reveal complex chemistry occurring in the icy mantles of dust grains and in the gas phase prior to and after the formation of protostars. The initial materials likely include hardy, refractory hydrocarbons inherited from the diffuse interstellar medium (*e.g.,* Pendleton and Allamandola, 2002) that contain a clear spectral signature of aliphatic hydrocarbon chains and other functional groups found in some primitive Solar System bodies (Alexander *et al.,* 2017). Pluto data currently available do not enable a conclusive search for such spectral signatures.

Laboratory studies of energetically processed interstellar ice analogs (*e.g.,* Allamandola *et al.,* 1988; Strazzulla and Baratta 1992; Greenberg *et al.,* 2000; Moore *et al.,* 2001) have shown that organic residues, which are analogous to tholins, are formed whether the energy emanates from UV light, charged particles, or thermal processes (Kebukawa and Cody, 2015). Outer Solar System planetesimals, and perhaps Pluto itself, formed in environments where one or more of those energetic processes was prevalent, and the initial starting materials that formed these planetesimals hold vital keys to the chemical complexity that would later occur. Thus, geological processes uncovering buried tholins on Pluto may be revealing organics of either early Solar System legacy or interior non-ocean processes, in addition to the sources prominent in this work.

The potential for some type of biological activity to be kindled on a body like Pluto is unknown, and even the potential for future biology on this and other small, frigid planets under warmer conditions provided during the red giant phase of stars like the Sun is currently unknowable, although speculation has been advanced (Stern, 2003). However, the primary near-term astrobiological significance of Pluto's chemical and geological complexity lay in the possibility that there are at least three pathways by which complex carbon-based compounds can be provided to life-bearing planets, and the preserved traces of these pathways may be discernable on a body like Pluto. Evidence for atmospheric, surface ice, liquid interior, and primordial endowments may all be present on Pluto and potentially other Kuiper Belt objects, providing fertile ground for investigation of the ideas that we advance here.

Complex organics that appear to emerge from Pluto's interior likely derive from material that was part of the feedstock from which planetesimals formed in the outer regions of the solar nebula. Future studies in the laboratory, with the James Webb Space Telescope, and someday with a spacecraft orbiting Pluto, should draw all of these threads together for a more comprehensive understanding of Pluto's prebiotic chemistry. Other Kuiper Belt planetary bodies observed from Earth show a range of color and spectroscopic characteristics (*e.g.,* Barucci *et al.,* 2008), and some of them, particularly the large ones, can reasonably be expected to share aspects of Pluto's chemical history.

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No competing financial interests exist for any author.

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